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# Quantification of Oil Recovery Efficiency, CO<sub>2</sub> Storage Potential, and Fluid-Rock Interactions by CWI in Heterogeneous Sandstone Oil Reservoirs

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## Abstract

Significant interest exists in improving recovery from oil reservoirs while addressing concerns about increasing CO<sub>2</sub> concentrations in the atmosphere. The combination of Enhanced Oil Recovery (EOR) and safe geologic storage of CO<sub>2</sub> in oil reservoirs is appealing and can be achieved by carbonated (CO<sub>2</sub>-enriched) water injection (CWI). So far, through several flooding experiments, the potential of carbonated water injection as an EOR scenario has been investigated. While several coreflood experiments on homogeneous cores have been performed, there is no information on the effectiveness of CWI for oil recovery and CO<sub>2</sub> storage potential on heterogeneous cores. Since not all the oil reservoirs are homogenous, understanding the potential of CWI as an integrated EOR and CO<sub>2</sub> storage scenario in heterogeneous oil reservoirs is essential.

With this objective, a series of high-pressure and high-temperature coreflood experiments were performed on a heterogeneous sandstone core. Based on the results, the heterogeneity of rock dominated water and carbonated water flow paths led to early breakthrough. However, interestingly, the ultimate oil recovery by CWI, either as the secondary or tertiary injection scenario, was higher than that of conventional waterflooding. Both secondary and tertiary CWI showed a strong potential for increasing oil recovery from the heterogeneous core and remobilized part of the trapped oil. In addition to the strong oil recovery by CWI, CWI demonstrated the good potential for safe underground storage of CO<sub>2</sub> in heterogeneous

reservoirs. Furthermore, carbonated water-sandstone rock interactions led to the slight mineral dissolution of the rock and separation of the submicron inorganic particles from the surface of the rock. These inorganic particles, which were previously interacting with asphaltenes and polar components of the oil during the ageing period, produced a hydrogen bond with water and formed oil in water emulsion. This phenomenon is called ‘Pickering emulsion’ which can lead to wettability alteration from oil-wet towards more water-wet conditions and in turn a better oil recovery by CWI.

## **Keywords**

EOR; CO<sub>2</sub> storage; new gaseous phase; mineral dissolution; Pickering emulsion.

## **1. Introduction**

As the CO<sub>2</sub> concentration in the atmosphere is increasing, interests for storing CO<sub>2</sub> in deep underground geological formations has been growing rapidly. One of the ideal candidates for underground storage of CO<sub>2</sub> is oil reservoirs. CO<sub>2</sub> storage in oil reservoir is economically interesting for the industry as the injected CO<sub>2</sub> can be applied for enhancing oil recovery. With this approach, different integrated Enhanced Oil Recovery (EOR) and CO<sub>2</sub> storage scenarios were developed. One of these integrated scenarios generating a lot of interest currently is carbonated (CO<sub>2</sub>-enriched) water injection, in which water as the carrier fluid, will displace the CO<sub>2</sub> inside the porous medium. As the CO<sub>2</sub>-enriched water comes into contact with the resided oil inside the reservoir, due to the higher solubility of CO<sub>2</sub> in oil than in water, strong partitioning of CO<sub>2</sub> between the phases (CW and oil) will take place.

CO<sub>2</sub> partitioning between carbonated water (CW) and the trapped oil would lead to a series of dynamic fluid-fluid interactions including the formation of the new gaseous phase<sup>1-4</sup>, oil swelling and oil viscosity reduction<sup>5-16</sup>. The two former mechanisms were already documented in the literature by several researchers<sup>5-16</sup>; however, the first mechanism; i.e. formation and

growth of the new gaseous phase, was documented by us for the first time in the literature. Through a series of integrated experiments<sup>1-4</sup>, we managed to reveal the crucial role of the formation and growth of the new gaseous phase on oil recovery by CWI under realistic reservoir conditions. Based on the results, the associated gas content of the reservoir oil plays a significant role in the oil recovery mechanisms of CWI. CO<sub>2</sub> partitioning between ‘live oil’ (oil with dissolved gases) and CW leads to the nucleation of a new gaseous phase inside the oil phase. According to the PVT results, the new gaseous phase is initially made of CH<sub>4</sub>, then over time becoming enriched with CO<sub>2</sub>. The high-pressure and high-temperature micromodel (direct visualization) findings<sup>1-4</sup> indicated that formation and continued growth of the new gaseous phase can lead to better oil recovery through (i) reconnection of the trapped oil and oil displacement, (ii) creating a favourable three phase flow region with less residual oil saturation, and (iii) restricting the flow path of CW and diverting it toward unswept areas of the porous medium.

So far, the potential of CWI for enhancing oil recovery and CO<sub>2</sub> storage has been studied through several coreflood experiments<sup>3-7,8,9,11,12,15,16</sup>. These experiments were performed under different experimental conditions including various pressures, temperatures, rock mineralogies and oil types. However, uniquely, all of these studies were performed in homogenous rocks and so far, in the literature, the potential of this integrated EOR and CO<sub>2</sub> storage scenario (CWI) in heterogeneous reservoirs has not been studied. As many major oil reservoirs in the world and, particularly, in the Middle East are either heterogeneous or fractured, understanding the true potential of CWI for these conditions is essential. To address this lack of crucial information, in this study, the potential of CWI for both enhancing oil recovery and CO<sub>2</sub> storage in a heterogeneous sandstone rock was investigated. A series of high-pressure high-temperature flooding experiments in a heterogeneous core were performed at an experimental pressure and

temperature of 2500 psia and 100 °F. Furthermore, it was attempted to study the fluid-sandstone rock interactions occurring during CWI.

## 2. Experimental Setup and Procedure

### 2.1. Core Flood Rig

The utilised experimental setup (Figure 1) was designed to conduct flooding experiments at high-pressure and high-temperature conditions. To minimise the gravity effect, the core holder was placed horizontally. The core holder, injection cells and back pressure are located inside an oven at a constant temperature of 100 °F. The core effluent fluids are passed through a back pressure regulator where the pressure would drop from 2500 psi to atmospheric pressure and hence, any dissolved CO<sub>2</sub> liberated. The separated liquid is then collected in a graduated cylinder while the CO<sub>2</sub> passes through a gasometer.

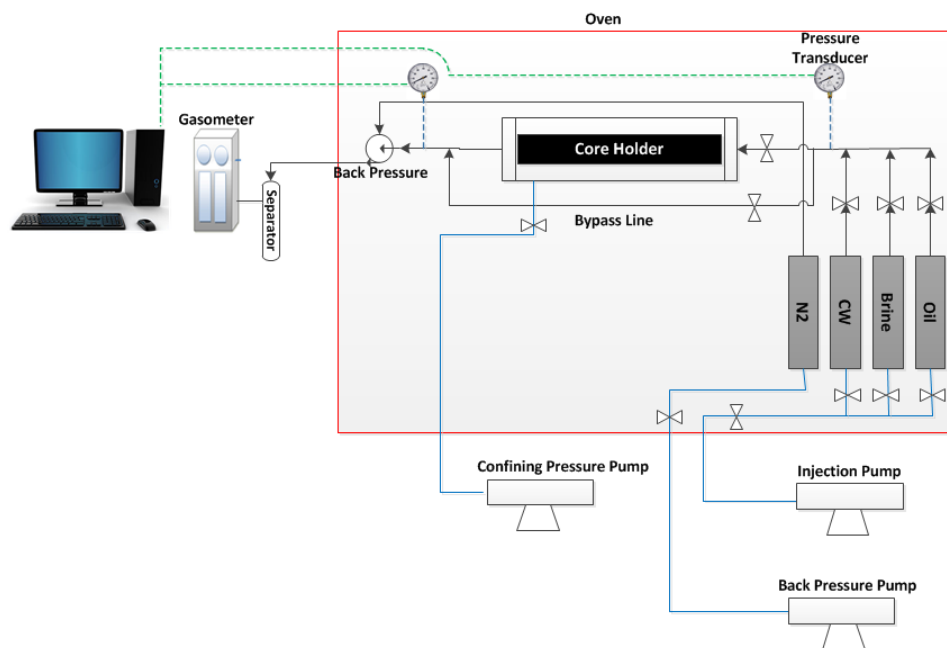


Figure 1: Schematic of the rig

### 2.2. Fluids Properties

Crude oil A with the API and density of 20.8° and 0.9286 gr/cm<sup>3</sup> was used (other properties of this crude are shown in Table 1). A synthetic sea brine with the salinity of 54,647 ppm was employed (Table 2) with the viscosity of the brine at test conditions of 0.789 cp. To prepare the carbonated (CO<sub>2</sub>-enriched) brine (CW), CO<sub>2</sub> was mixed with the brine at experimental pressure and temperature (2500 psi and 100 °F). The CO<sub>2</sub> content of carbonated brine was measured as 26.8 scc CO<sub>2</sub>/scc brine.

**Table 1.** Crude A properties

crude ID	API	saturates (wt. %)	aromatics (wt. %)	resins (wt. %)	asphaltenes (wt. %)
A	20.8	30.00	40.10	24.20	5.70

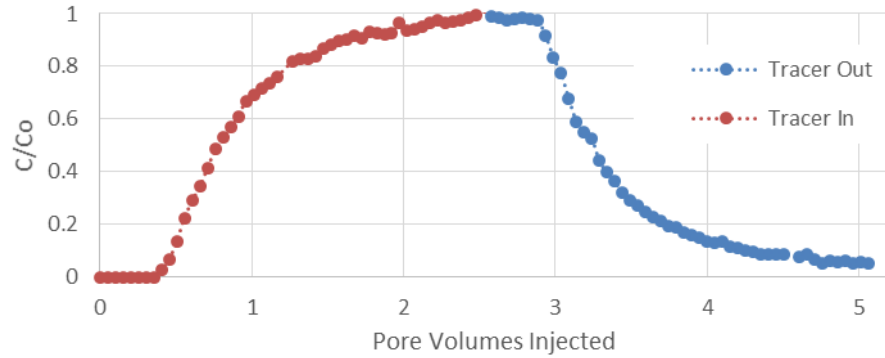
**Table 2.** Ionic composition of the seawater

ion	ppm
Na	16844
Ca	664
Mg	2279
SO <sub>4</sub> <sup>-2</sup>	3560
Cl	31107
HCO <sub>3</sub> <sup>-1</sup>	193

### 2.3. Core Properties

A heterogeneous sandstone core was utilised with the porosity of the core initially determined by helium and then confirmed later by a brine porosity test. To be sure that the core was heterogeneous, miscible tracer test was performed in the form of Lithium. Figure 2 depicts the changes in lithium concentration during the tracer test. The gradual rise and the long decreasing tail in the lithium concentration profile confirm that the core is heterogeneous. Furthermore, CT-scanning analysis was carried out on the core in order to see heterogeneities, such as permeability layers present in the core. The result of core scanning (Figure 3) indicates the bedding and heterogeneity of the core. The scan was performed along the long axis of the core.

Figure 3A indicates the long axis of the core when it was viewed normally, and Figure 3B presents the long axis of the core when the data is levelled. The dimensions and other physical properties of the core are given in Table 3.



**Figure 2:** Results of the Lithium tracer test in heterogeneous sandstone core



**Figure 3:** CT-Scan results of the core

To have a complete understanding of mineralogy of the utilised sandstone rock, XRD analysis was carried out on a slice of the rock. The result of the XRD analysis indicates that 99.7% of the rock is made of silica oxide (Quartz) and the rest is Greenalite which is a mineral in the kaolinite (clay) group.

**Table 3:** Dimensions and properties of the core used in the study

core	length (cm)	diameter (cm)	porosity	absolute K (mD)	pore volume
sandstone	30.5	4.942	17.68%	98.73	102.108

## 2.4. Methodology

Having cleaned the core and measured its pore volume, porosity and permeability, initial water saturation ( $S_{wi}$ ) was established in the core through a drainage process of the brine-saturated cores firstly with several heavy mineral oils and lastly crude oil (i.e., displacement of brine with oil). The core was aged in crude A for a period of three weeks at a temperature of 194 °F. The higher temperature was chosen as to accelerate the ageing process. After the ageing period, live oil was injected into the core to displace the dead oil. The live oil is a mixture of methane and crude A with the gas oil ratio (GOR) of 50 scc CH<sub>4</sub>/cc oil. Once total displacement of the dead oil with live oil, the core was ready for the experiments.

Experiment number one was a secondary conventional waterflooding (WF) followed by a tertiary carbonated water injection (CWI). To simulate conventional WF in an oil reservoir, a period of methane-saturated brine injection (WF) was conducted until no more oil was produced. Since the live oil was saturated with methane, the brine was pre-equilibrated with methane at test conditions to prevent methane mass transfer between the brine and live oil during the experiment. The methane content of brine was measured and it was 3 scc CH<sub>4</sub>/cc brine. Through this stage, the volume of effluent fluids was recorded to calculate the recovery of WF as a secondary recovery method. The conditions of the core at this stage of the test would represent a water-flooded heterogeneous oil reservoir in which significant amount of oil still exists in the form of immobile disconnected patches of oil. Most oil reservoirs are abandoned at this stage unless an EOR method can be justified on both technical and economic grounds. To examine the potential of CWI as the tertiary injection scenario, at the end of WF period, CWI began with the same injection rate and flow direction as the preceding WF.

Experiment number two was secondary CWI. Both experiments were performed at pressure and temperature of 2500 psi and 100 °F. The rate of injection for all aforementioned experiments was 5 cm<sup>3</sup>/hr. Table 4 summarises the coreflood experiments.



**Table 4:** Summary of Coreflood experiments and their conditions

Test	Injection Scenario	Core	Oil	Temp. (F)	Press. (psi)
1	WI → CWI	Sandstone	Crude A (live – Fully Saturated)	100	2500
2	CWI	Sandstone	Crude A (live – Fully Saturated)	100	2500

### 3. Experimental Results and Discussion

#### 3.1. Conventional WaterFlooding

Figure 4 depicts the oil recovery profile which was obtained during both water injection and tertiary CWI. Around 2 PV (Pore Volume) of methane-saturated brine injection (blue curve), recovered 34.9% of the original oil in place (OOIP) leaving 0.46 PV of residual oil after waterflooding. Water breakthrough (BT) happened at 0.21 PV of injection. The main reason for the early breakthrough of brine was the heterogeneity of the rock. Due to the presence of a high permeability layer in the rock, water tended to flow through the theft zone and tended to reduce front advancement in the lower permeability layer. As a result, BT happened early leaving a large volume of bypassed or virgin oil (untouched oil) remaining in the rock.

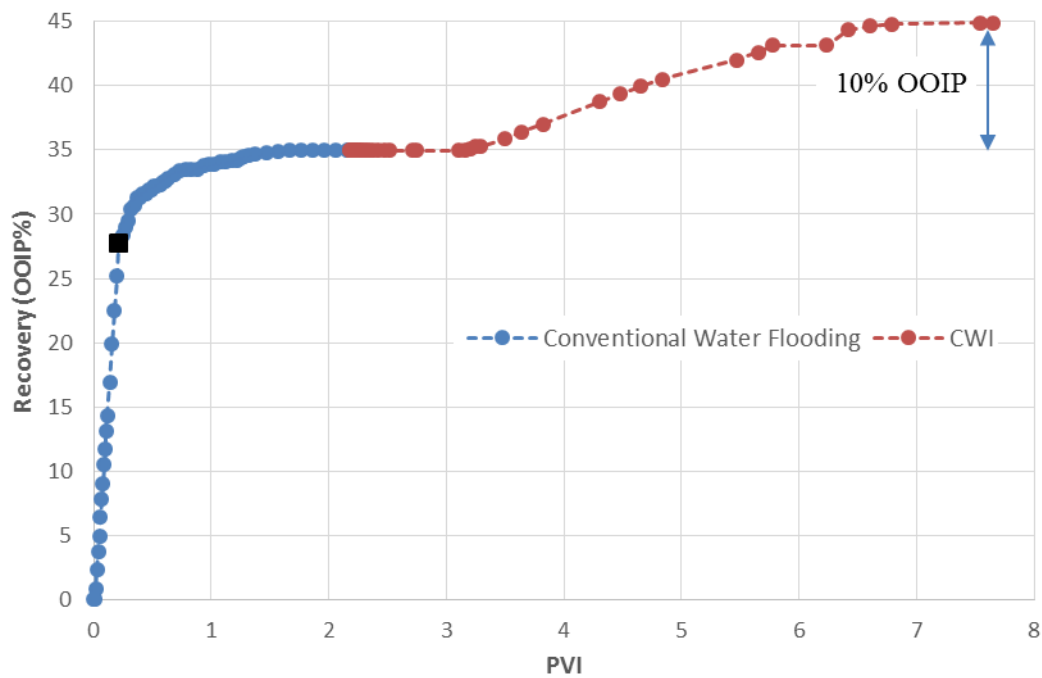
Although breakthrough happened at early pore volumes of injection, there was still oil recovery after breakthrough. As indicated in Figure 4, recovery factor after breakthrough increased from 27.8% to 34.9% OOIP. As presented in Figure 4, the amount of produced oil after 1 PV of injection is very small and converged to zero at around 1.5 PV of injection.

To study the potential of CWI as a tertiary injection method in waterflooded heterogeneous reservoirs, at the end of the WF period, CWI began with the same injection rate and the same flow direction as the preceding WF. The red curve in Figure 4 presents the oil recovery profile obtained during tertiary CWI. The injection of CW after waterflooding gradually increased the amount of oil recovery and finally led to the production of 10% of the original oil in place (OOIP). This significant additional oil recovery by CWI reveals the strong potential it may have as a tertiary injection scenario in waterflooded heterogeneous oil reservoirs where the direct displacement of oil by water is usually poor. The main reasons for this additional recovery are:

- I. Formation of the new gaseous phase as a result of CO<sub>2</sub> partitioning between CW and live oil. For the first time in the literature, based on a series of integrated micromodel, coreflood and PVT studies<sup>1-4</sup>, we disclosed that CO<sub>2</sub> partitioning between CW and live oil leads to the formation of a new gaseous phase inside the oil that plays the dominant role in oil recovery by CWI. Based on our most current studies<sup>1-4</sup>, the formation of new gaseous phase can lead to better oil recovery through (i) reconnection of the trapped oil and oil displacement, (ii) creating a favourable three phase flow region with less residual oil saturation, and (iii) restricting the flow path of CW and diverting it toward unswept areas of the porous medium.
- II. Wettability alteration. Based on the results of our wettability studies<sup>17,18</sup>, CW due to its acidic nature has the potential to alter the wettability of mixed-wet quartz toward more water-wet conditions. The main component of the core applied in this study is quartz, therefore, CWI can influence its wettability state. Wettability alteration by CW can directly affect the pore displacement mechanism and fluid distribution inside the porous medium and therefore leads to better oil recovery.

III. Oil viscosity reduction as a result of CO<sub>2</sub> mass transfer from CW into the bypassed oil.

The strength of this mechanism compared to the two others is less as the utilised live oil has a low oil viscosity of around 14 cp. Oil viscosity reduction by CWI is more pronounced for medium to heavy oils<sup>6,10,11</sup>.

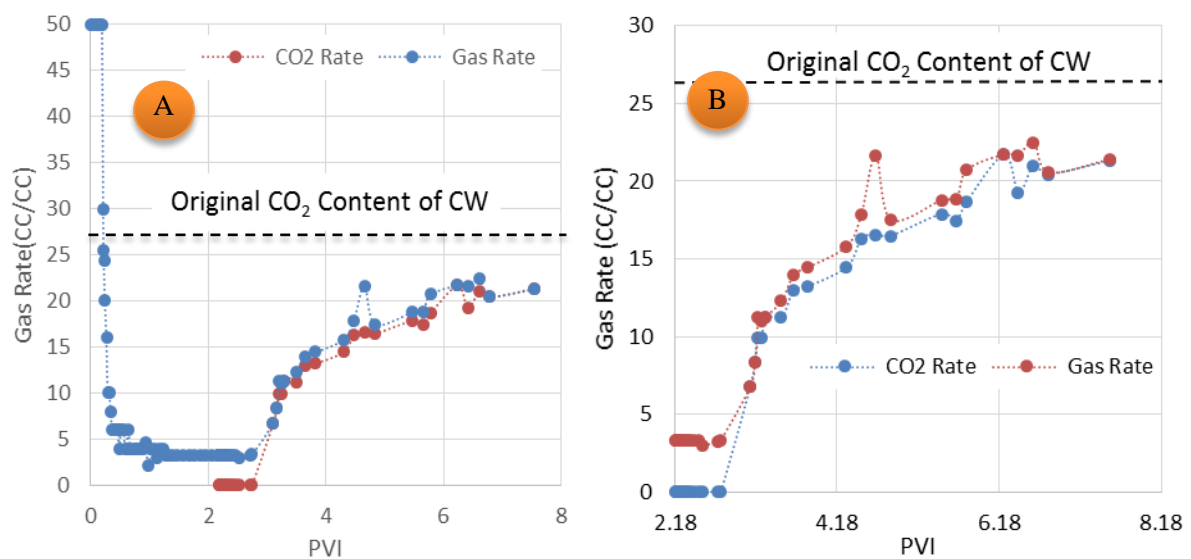


**Figure 4:** Measured cumulative oil recovery during conventional WF and subsequent CWI in the heterogeneous sandstone core at 100 F and 2500 Psia.

Figure 5A depicts the rate of gas production and the calculated rate of CO<sub>2</sub> production during the period of WF and subsequent CWI. This figure represents the promising potential of CWI for safe underground storage of CO<sub>2</sub>. About 44% of the injected CO<sub>2</sub> during tertiary CWI period was stored in the core through dissolution trapping mechanism which is one of the safest methods for safe underground storage of CO<sub>2</sub>.

Figure 5B depicted the rate of gas production and calculated rate of CO<sub>2</sub> production during tertiary carbonated water injection. This was done to check whether the fluids (mostly residual

oil) inside the core were almost saturated or still taking up  $\text{CO}_2$  from the injected CW. As mentioned above, the original  $\text{CO}_2$  content for CW was 26.8 scc  $\text{CO}_2/\text{cc}$  brine. This ratio was monitored through the test and after 5.4 PV of CWI, the ratio reached 80% of the original value. It is desirable to stop the CW injection when the residual oil in the core is almost saturated with  $\text{CO}_2$ , i.e. when  $\text{CO}_2$  gas rate reaches close to its injected value. This would represent the maximum oil that can be recovered from the CWI implementation as well as the maximum  $\text{CO}_2$  that can be stored in the oil and brine within the core.



**Figure 5:** Rate of gas production and calculated rate of  $\text{CO}_2$  production during WI and subsequent CWI

### 3.2. Secondary Carbonated Water Injection (CWI)

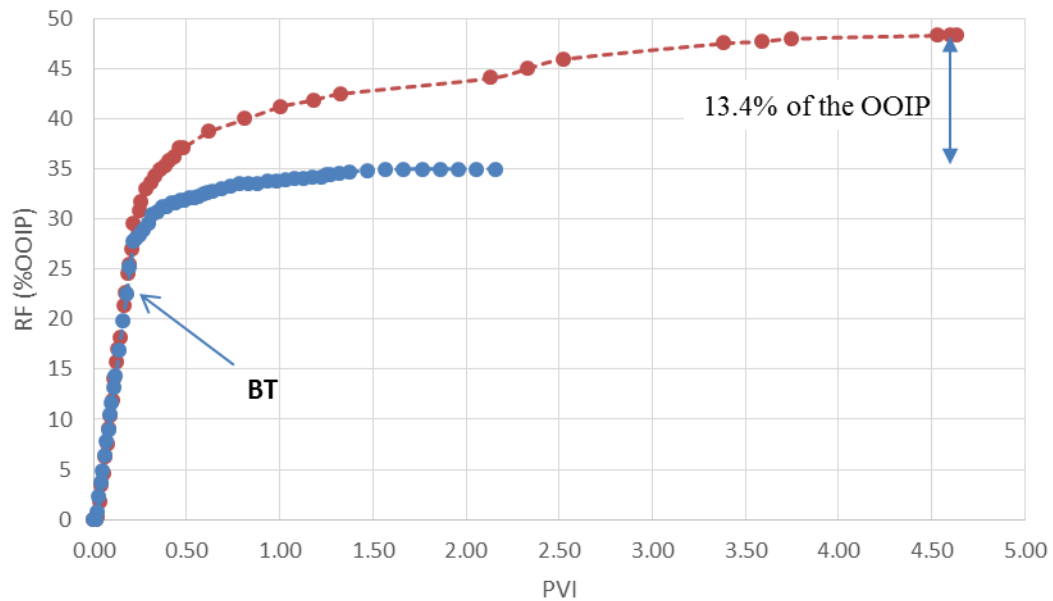
Figure 6 compares oil recovery profiles obtained by the secondary water injection (Experiment 1) and secondary carbonated water injection, keeping all other parameters the same. As depicted in Figure 6, secondary water injection in experiment number one resulted in oil recovery of 34.9% of the original oil in place (OOIP). However, CWI as a secondary recovery method in experiment number two led to oil recovery of 48.4% of the OOIP. These results

clearly verify the strong potential of CWI as a secondary recovery method in comparison to waterflooding in heterogeneous reservoirs.

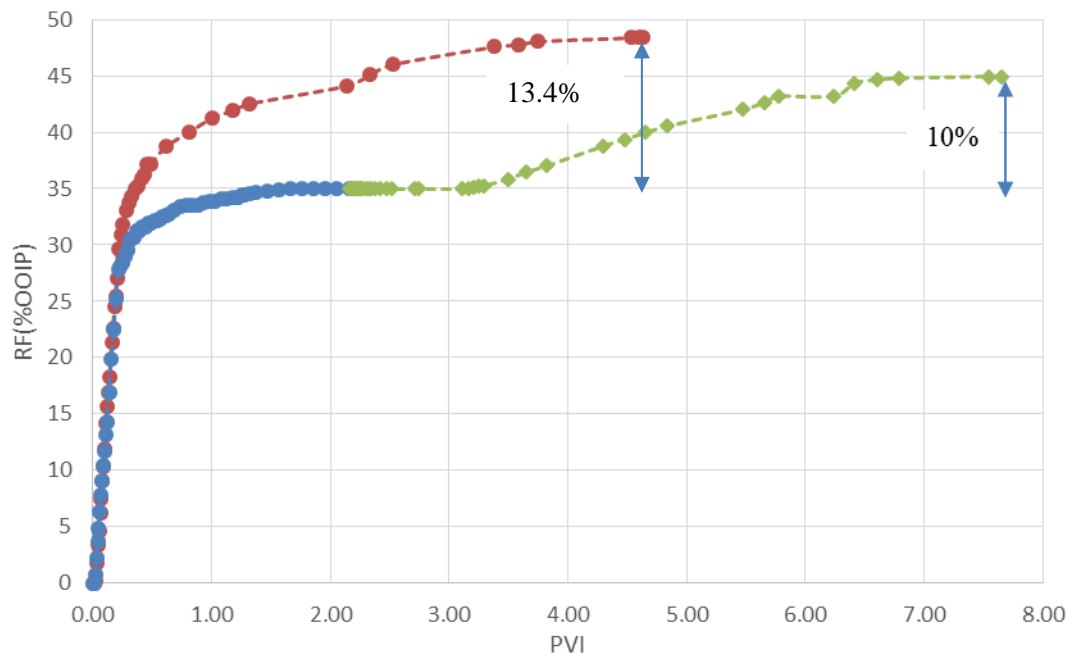
Water breakthrough (BT) for both cases occurred at 0.21 pore volume of injection, with early water breakthrough being attributed to the heterogeneity of the rock. Reservoir heterogeneity dominated the flowing path of brine and CW, which led to this early breakthrough. Due to the presence of the high permeability layer in the rock, water or carbonated water tended to flow through it. This resulted in early BT and a large volume of bypassed or virgin oil (untouched oil) remaining in the rock. Although in both experiments BT happened at early in terms of injection, oil production continued in both experiments after the BT. As depicted in Figure 6, for the case of conventional waterflooding, recovery factor after BT increased by 7% of the OOIP. Interestingly, for the case of secondary CWI, recovery factor after BT increased by 18.8% of the OOIP. The same reasons, which led to additional oil recovery by tertiary CWI in experiment number one, are attributed for this significant increase in oil recovery after carbonated water BT and finally better performance of secondary CWI compared to the secondary conventional waterflooding counterpart.

Figure 7 summarised the strong potential of CWI either as a secondary or tertiary injection scenario in the heterogeneous sandstone rock. Based on this figure, CWI in heterogeneous sandstone rock, compared to conventional waterflooding, improved oil recovery in both secondary (pre-waterflood) and tertiary (post-waterflood) injection modes. However, the results showed the stronger potential of CW when it is injected as a secondary recovery mode. It should also be noted that the number of pore volumes of injected CW during the secondary scenario was less than that during tertiary scenario. The main reason for increased performance of secondary CWI over tertiary is the presence of lower amounts of water in place during secondary than tertiary CWI. In tertiary CWI, the injected CW needs to displace the previously

injected plain water inside the core in order to come in contact with resided oil and this will negatively affect the oil recovery mechanisms of CWI.



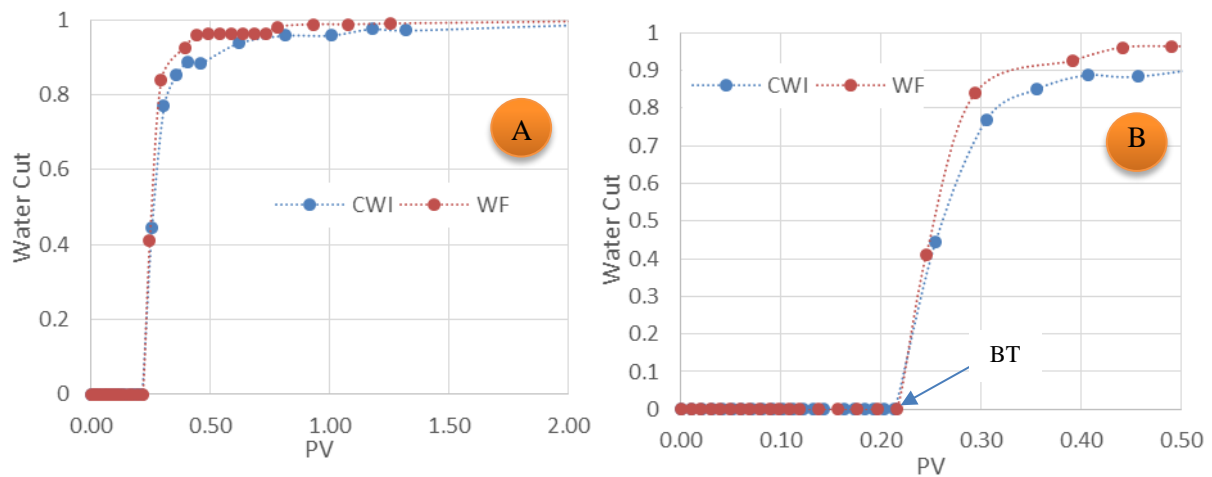
**Figure 6:** Comparison of the performance of a secondary CWI in the heterogeneous core with its secondary water injection counterpart



**Figure 7:** Oil recovery through experiments number one and two in heterogeneous sandstone rock

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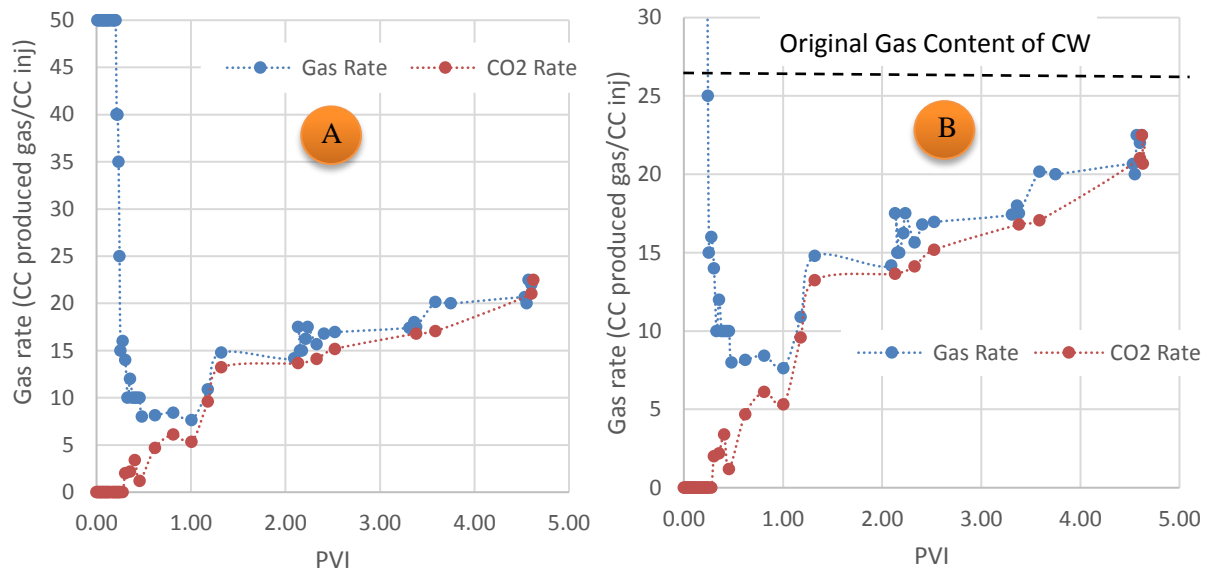
244 Figure 8A compares the water cut during secondary CWI in the heterogeneous core with its  
245 secondary water injection counterpart. As depicted in this figure, CWI reduced the water cut  
246 and improved the water conformance. Figure 8B shows a magnified version of the data  
247 presented in Figure 8A which highlights the differences between water cuts during CWI and  
248 WI after the water breakthrough (BT). This figure clearly indicates a better conformance  
249 control for the case of CWI than waterflooding in the heterogeneous rock.



250 **Figure 8:** Comparison of water cut during secondary CWI in the heterogeneous core with its  
251 secondary water injection counterpart

252 Figure 9 depicts the rate of gas production and calculated rate of CO<sub>2</sub> production during  
253 secondary carbonated water injection. Based on Figure 9, the initial gas production rate during  
254 secondary CWI was constant and was equal to gas oil ratio (GOR) of produced live oil. After  
255 breakthrough, the gas rate dropped. Since after BT there was oil production, methane gas from  
256 the produced oil was released. Moreover, BT of CW caused the production of CO<sub>2</sub> gas.  
257 According to Figures 9A and B, secondary CWI demonstrated a good potential for safe CO<sub>2</sub>  
258 storage. About 47.5% of the injected CO<sub>2</sub> was stored inside the core at the end of secondary  
259 CWI. This value for the tertiary CWI was 44%. These results verified the strong potential of

CWI for safe underground storage of CO<sub>2</sub> in oil reservoirs. As mentioned earlier, the original CO<sub>2</sub> content of CW was 26.8 scc CO<sub>2</sub>/cc brine. This ratio was monitored through the experiment (Figure 9) and after 4.63 pore volume of injection, the ratio reached to 84% of the original value. This indicates that the resided fluids (mostly oil) are yet taking CO<sub>2</sub> from the injected CW.



**Figure 9:** Gas rate during secondary carbonated water injection in a heterogeneous sandstone rock

### 3.3. Ion Chromatography Analysis

During both experiments, several brine samples were taken from the effluent fluid to study the rock-fluid interactions during both waterflooding and CWI. The ion composition of the collected brine samples was analysed by Ion Chromatography (IC) analysis. The results were compared with the result of the stock sample (original brine).

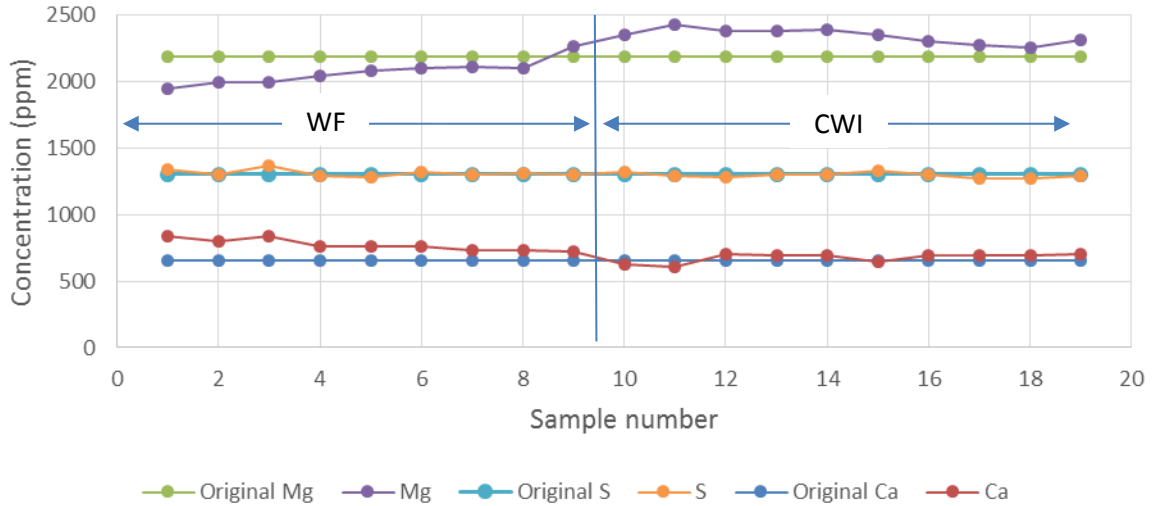
Figure 10 presents the results of IC analysis for Ca, Mg and S in experiment number 1 in which a secondary waterflooding was followed by a tertiary CWI. Based on this figure, during secondary waterflooding, the concentration of Ca in the effluent brine was slightly higher than



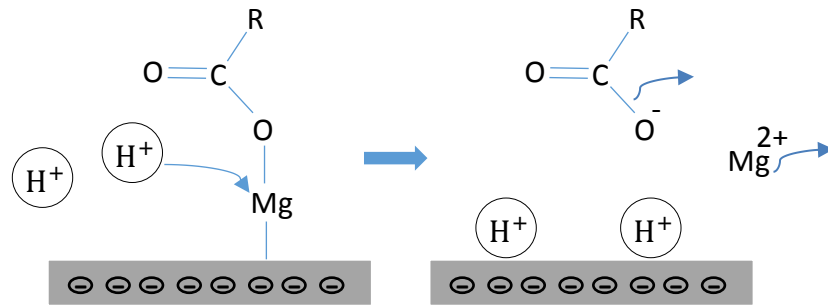
276 the concentration of Ca in original brine. Conversely, the concentration of Mg ion in the effluent  
 277 brine was lower than its original value in the stock sample. This behaviour is attributed to the  
 278 higher affinity of Mg compare to Ca toward this rock type. As a result of this higher affinity,  
 279 during flooding, Mg cations took the place of Ca.

280 Based on Figure 10, during tertiary CWI period the concentration of Mg ion in the effluent  
 281 brine was slightly higher than its original concentration; however, the concentrations of Ca and  
 282 S were not changed. This behaviour is due to the presence of higher amounts of  $H^+$  in brine  
 283 (see reactions 1 to 3) during tertiary CWI period than conventional waterflooding. As a  
 284 consequence, the mineral surface exchanges  $H^+$  (existed in carbonated brine) with previously  
 285 adsorbed cations. This mechanism is called ion exchange. During CWI, dependent on the rock  
 286 type, ion exchange may occur between the minerals and CW. Mg ions, which already occupied  
 287 most of the exchangeable positions during WF period, were exchanged by  $H^+$  ions of the  
 288 injected CW. As a result of this ion exchange, the concentration of Mg in effluent brine was  
 289 increased during tertiary CWI. Furthermore, this ion exchange leads to the breakage of the  
 290 bonds between the acidic components of the oil and the negatively charged rock's surface  
 291 which in turn leads to wettability change from oil-wet toward more water-wet conditions and  
 292 therefore better oil recovery (Figure 11)<sup>17</sup>.





**Figure 10:** IC results of Ca, Mg, and S ions during experiment number 1

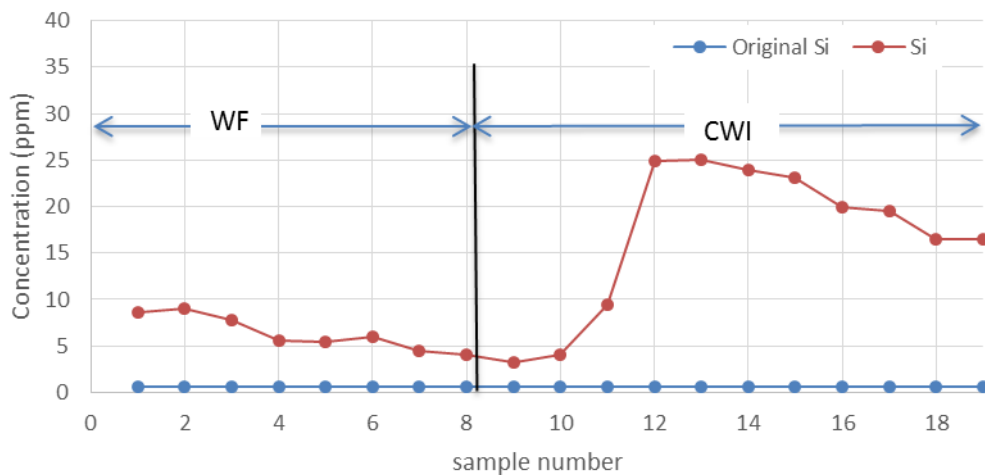


**Figure 11:** Ion exchange process that leads to desorption of acidic components of the oil from the rock surface and therefore wettability alteration toward more water-wet conditions during CWI

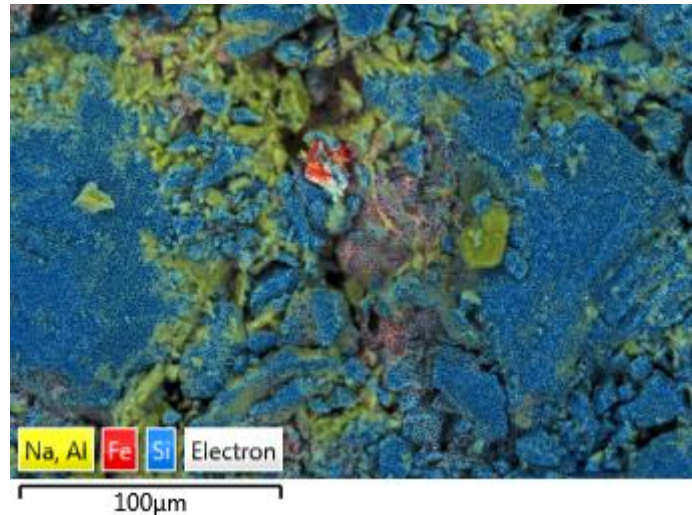
Figure 12 depicts the concentration of Si in effluent brine before and after CWI. As indicated in this figure, during waterflooding (WF) the concentration of Si in effluent brine was slightly higher than its original value in the stock sample. This behaviour can be explained based on the rock mineralogy. The XRD results indicated that 97% of the rock is made of silica oxide and the rest is Greenalite which is a clay mineral. Furthermore, performed SEM analysis on the rock surface (Figure 13) confirmed the XRD results and indicated the rock is quartz sandstone with some Clays and Fe-rich particles. More SEM images from different points on

the rock revealed that the rock is mainly composed of Si, Al, Fe, Mg and C components. Clay minerals can react with seawater and as a result of this reaction, small amounts of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  are dissolved into the seawater. This could be the reason for slightly higher Si concentration in effluent brine compared to stock sample during waterflooding stage (Figure 12).

As seen from Figure 12, during tertiary CWI the concentration of Si in the effluent brine was slightly higher than its original value in the stock sample. This increase in silica concentration is due to the acidic nature of CW which under these test conditions led to slight mineral dissolution. Mineral dissolution can also lead to precipitation of some of the minerals in the porous medium and therefore drop in permeability. The absolute permeability of utilized core in this study was reduced by around 6% of the original value after the first experiment.

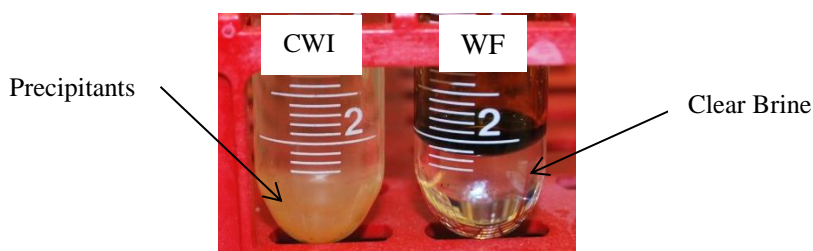


**Figure 12:** IC results of Si during experiment number 1

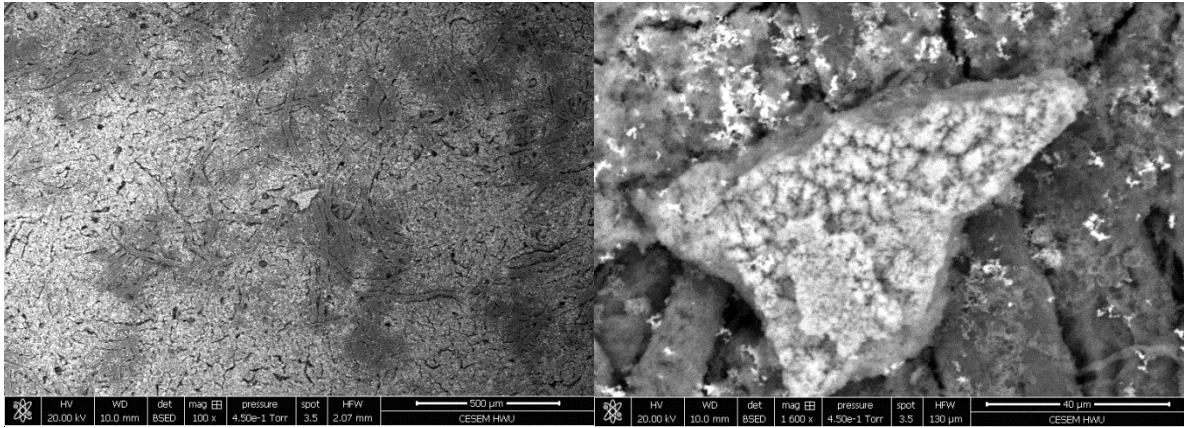


**Figure 13:** SEM image of the rock

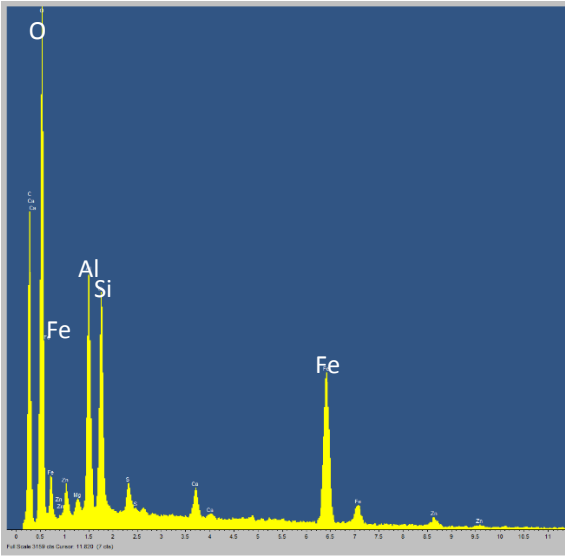
It was noted in experiment number 1, when tertiary CWI was started, after a while small amounts of precipitations in the effluent fluid were observed. Figure 14 presents two effluent samples, one collected at around 1.2 pore volumes of tertiary CWI and the other one collected at around 0.24 pore volumes of secondary waterflooding. The brine sample taken during the waterflooding period is clear; however, the one taken during tertiary CWI has a small amount of precipitation. These precipitants were collected and analysed by SEM. The SEM analysis revealed the presence of Si, Al, and Fe (Figures 15 and 16). This analysis coupled with IC analysis verified the potential of CWI for slight mineral dissolution of sandstone rocks. This slight mineral dissolution can help in detachment of oil aggregates from the rock surface and consequently extra oil recovery. Additionally, this can help to wettability alteration of the rock toward more water wet conditions<sup>17</sup>.



**Figure 14:** Brine samples collected at the time of secondary waterflooding and tertiary CWI



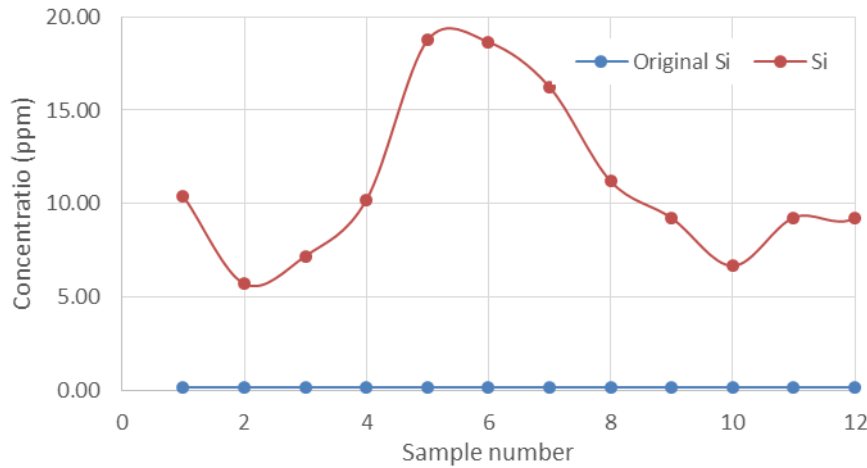
**Figure 15:** SEM image of the precipitants



**Figure 16:** SEM analysis of the precipitants

The IC results of Si in experiment number 2 verified the slight mineral dissolution of sandstone rock at the presence of CO<sub>2</sub>-enriched water. Figure 17 presents the concentration of Si in effluent brine during secondary CWI in experiment number 2 in comparison with its original value. As seen from Figure 17, the acidic nature of CW led to the slightly higher concentration

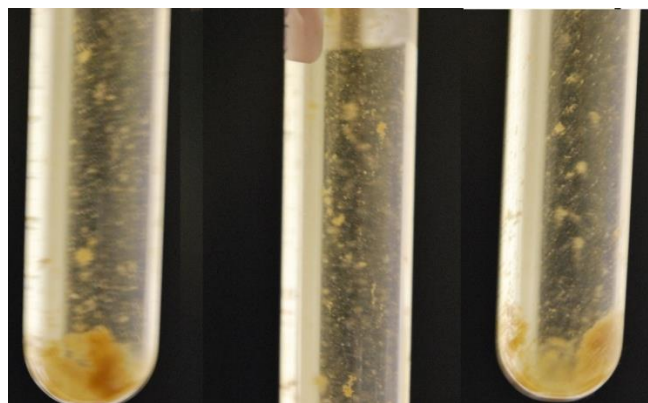
of Si in effluent brine compared to its original concentration. This demonstrated the potential of CW for minor mineral dissolution in sandstone cores.



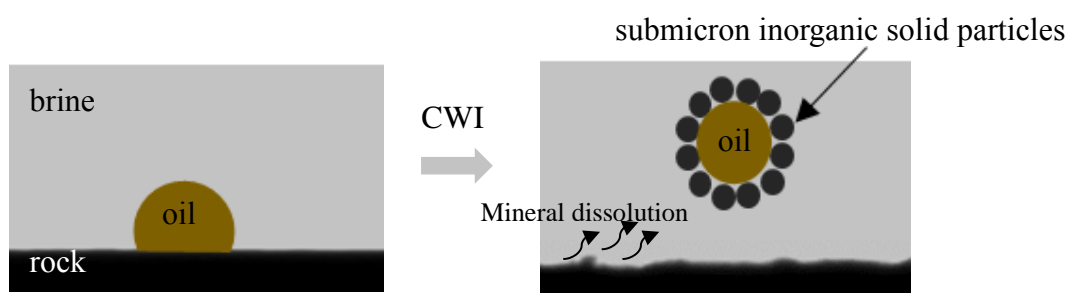
**Figure 17:** IC results for Si during experiment number 2

During both experiments, unstable oil in water emulsion was observed during final pore volumes of CWI. Experiment number 2 (secondary CWI), showed this after around 1.32 pore volumes of CWI (Figure 18). Three samples of the effluent brine were collected and filtered with the residue sent for SEM analysis. The samples were collected between 2.52 to 4.6 pore volumes of CW injection. Figure 18 depicts a brine sample from experiment 2 which shows the oil in water emulsions. The SEM analysis (Figure 20A) revealed that those emulsions were very small  $\text{Fe}_2\text{O}_3$  and Silica ( $\text{SiO}_2$ ) particles, that are surrounded by the oil droplets. Sulphur and traces of C and O in the SEM analysis come from the paper filter (Figure 20B). As mentioned earlier the slight mineral dissolution by carbonated water was verified in both experiments (see Figures 12 and 17). Additionally, a small amount of precipitations in effluent brine was also observed in both experiments (see Figures 15 and 16). Based on these results and observations, we can infer these submicron inorganic solid particles were coming from the rock. Oxygen atoms on the surface of the  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  particles provide sites for bonding with asphaltenes and polar components of the oil. During the ageing process, by isolating the

surface of the rock from the formation water, the adsorption sites were available to interact with asphaltenes and polar components of the oil. When CWI was started, due to its acidic nature, these submicron inorganic particles were leaving the rock surface (mineral dissolution). Next, this inorganic particle made a hydrogen bond with water and formed the oil in water emulsion (Figure 19). This phenomenon is called ‘Pickering emulsion’ that can lead to a better oil recovery.



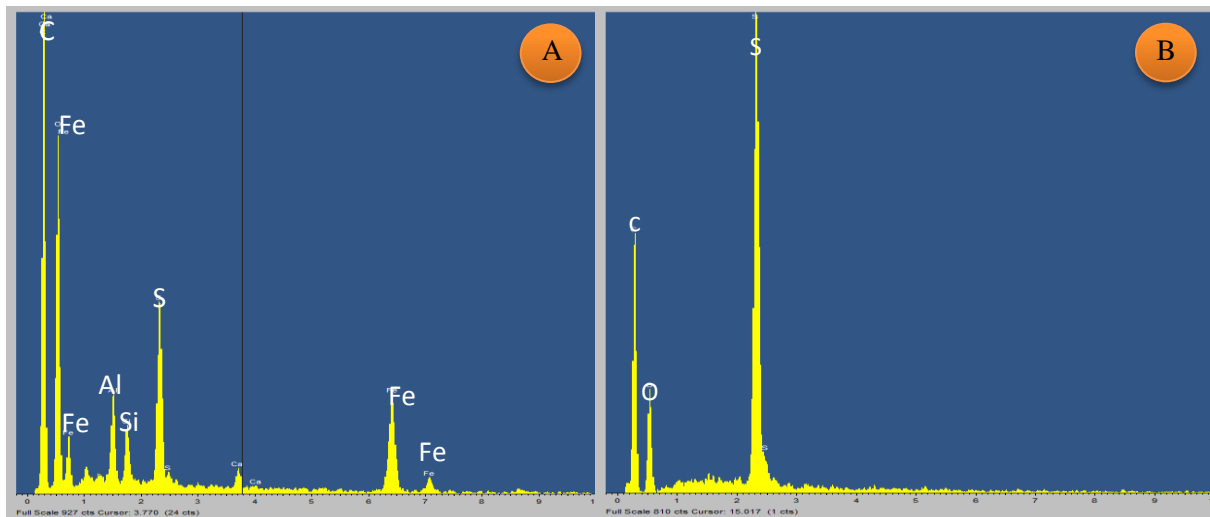
**Figure 18:** Oil-in-water emulsion at the end of CWI in experiment number 2



**Figure 19:** Acidic nature of CW that leads to slight mineral dissolution and therefore formation of oil in water Pickering emulsion.

It should be noted that although during waterflooding period (experiment 1) slight mineral dissolution would have occurred (Figure 12), no evidence of oil in water emulsion was

observed. The reason that emulsion is only formed during CWI is due to the low pH of CW. Low pH favours emulsion formation<sup>19</sup>. As indicated in Figure 18, with time, larger particles agglomerate and precipitate. At high particle concentrations, particles can agglomerate and form larger structures with entrained asphaltenes and water. This agglomeration might be caused by particle bridging due to either adsorbed asphaltene aggregates or the high surface energy of inorganic particles. The large agglomerates have a larger sedimentation velocity than the individual particles and require larger forces to hold them at the interface. Finally, with time the large agglomerates are precipitated.



**Figure 20:** SEM analysis of A) the observed emulsions during CWI and B) of the clean paper filter

#### 4. Conclusion

Due to the presence of the high permeability layer in the heterogeneous rock, water/CO<sub>2</sub>-enriched water tended to flow through the theft zone and reduce front advancement in the lower permeability layer. As a consequence, the early breakthrough of water happened during both waterflooding and CWI. However, interestingly, the ultimate oil recovery by CWI either as the tertiary or secondary injection scenario, in the heterogeneous rock, was much higher than that



of conventional waterflooding. The results indicate that CWI, in the heterogeneous rock, shows stronger recovery potential when it is injected as the secondary recovery mode rather than tertiary. Stronger oil recovery by CWI in the heterogeneous porous medium compared to waterflooding is mainly attributed to i. formation and growth of the new gaseous phase, and ii. wettability alteration. Based on the flooding results, CWI presented a better conformance control than waterflooding in the heterogeneous rock. Furthermore, the results revealed the strong potential of CWI for the safe underground storage of CO<sub>2</sub> in heterogeneous oil reservoirs. At the end of secondary and tertiary CWI, around 47.5% and 44% of the injected CO<sub>2</sub> was stored inside the heterogeneous core respectively. Furthermore, analysis of the produced brine samples during CWI in the heterogeneous sandstone core indicated the presence of slight mineral dissolution. According to the results, when CWI was started, due to its acidic nature, the submicron inorganic particles were coming off from the rock surface (mineral dissolution). These inorganic particles, which during aging were already interacting with asphaltenes and polar components of the oil, made a hydrogen bond with water and formed the oil in water emulsion. This phenomenon is called “Pickering emulsion” that can lead to a better oil recovery.

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## Reference

1. Seyyedi M, Mahzari P, Sohrabi M. An integrated study of the dominant mechanism leading to improved oil recovery by carbonated water injection. *J Ind Eng Chem*.

- 428 2017;45:22-32. doi:10.1016/j.jiec.2016.08.027.
- 429 2. Seyyedi M, Sohrabi M. Pore-Scale Investigation of Crude Oil/CO<sub>2</sub> Compositional  
430 Effects on Oil Recovery by Carbonated Water Injection. *Ind Eng Chem Res.*  
431 2017;acs.iecr.6b04743. doi:10.1021/acs.iecr.6b04743.
- 432 3. Seyyedi M, Sohrabi M, Sisson A. Experimental Investigation of the Coupling Impacts  
433 of New Gaseous Phase Formation and Wettability Alteration on Improved Oil Recovery  
434 by CWI. *J Pet Sci Eng.* 2016. doi:10.1016/j.petrol.2016.11.016.
- 435 4. Sohrabi M, Emadi A, Farzaneh SA, Ireland S, Oil E. A Thorough Investigation of  
436 Mechanisms of Enhanced Oil Recovery by CWI. 2015. doi:10.2118/175159-MS.
- 437 5. Sohrabi M, Riazi M, Jamiolahmady M, Kechut NI, Ireland S, Robertson G. Carbonated  
438 Water Injection (CWI) - A productive way of using CO<sub>2</sub> for oil recovery and CO<sub>2</sub>  
439 storage. *Energy Procedia.* 2011;4:2192-2199. doi:10.1016/j.egypro.2011.02.106.
- 440 6. Riazi M, Sohrabi M. Oil recovery improvement using CO<sub>2</sub>-enriched water injection.  
441 *SPE Eur Annu Conf Exhib.* 2009.
- 442 7. Sohrabi M, Tavakolian M, Emadi A, Jami M, Ireland S. Improved Oil Recovery and  
443 Injectivity By Carbonated Water Injection. 2012:1-12.
- 444 8. Kechut NI, Riazi M, Sohrabi M, Jamiolahmady M. Tertiary Oil Recovery and CO<sub>2</sub>  
445 Sequestration by Carbonated Water Injection (CWI). *SPE Int Conf CO<sub>2</sub> Capture,  
446 Storage, Util.* 2013. doi:10.2118/139667-MS.
- 447 9. Sohrabi M, Kechut NI, Riazi M, Jamiolahmady M, Ireland S, Robertson G.  
448 Coreflooding Studies to Investigate the Potential of Carbonated Water Injection as an  
449 Injection Strategy for Improved Oil Recovery and CO<sub>2</sub> Storage. *Transp Porous Media.*

- 2012;91(1):101-121. doi:10.1007/s11242-011-9835-5.
10. Riazi M, Sohrabi M, Jamiolahmady M. Experimental Study of Pore-Scale Mechanisms of Carbonated Water Injection. *Transp Porous Media*. 2011;86(1):73-86. doi:10.1007/s11242-010-9606-8.
  11. Kechut NI, Sohrabi M, Jamiolahmady M. Experimental and numerical evaluation of carbonated water injection (CWI) for improved oil recovery and CO<sub>2</sub> storage. *SPE Eur Annu Conf Exhib*. 2011.
  12. Shu G, Dong M, Chen S, Luo P. Improvement of CO<sub>2</sub> EOR performance in water-wet reservoirs by adding active carbonated water. *J Pet Sci Eng*. 2014;121:142-148. doi:10.1016/j.petrol.2014.07.001.
  13. Zuo L, Benson SM. Exsolution enhanced oil recovery with concurrent CO<sub>2</sub> sequestration. *Energy Procedia*. 2013;37:6957-6963. doi:10.1016/j.egypro.2013.06.629.
  14. Zuo L, Zhang C, Falta RW, Benson SM. Micromodel investigations of CO<sub>2</sub> exsolution from carbonated water in sedimentary rocks. *Adv Water Resour*. 2013;53:188-197. doi:10.1016/j.advwatres.2012.11.004.
  15. Martin JW. Additional oil production through flooding with carbonated water. *ProdMon*. 1951.
  16. Mosavat N, Torabi F. Experimental evaluation of the performance of carbonated water injection (CWI) under various operating conditions in light oil systems. *Fuel*. 2014;123:274-284. doi:10.1016/j.fuel.2014.01.077.
  17. Seyyedi M, Sohrabi M, Farzaneh A. Investigation of Rock Wettability Alteration by

- 472 Carbonated Water through Contact Angle Measurements. *Energy and Fuels*.  
473 2015;29(9):5544-5553. doi:10.1021/acs.energyfuels.5b01069.
- 474 18. Seyyedi M, Sohrabi M. Enhancing Water Imbibition Rate and Oil Recovery by  
475 Carbonated Water in Carbonate and Sandstone Rocks. *Energy and Fuels*.  
476 2016;30(1):285-293.
- 477 19. Wang X, Alvarado V. SPE 115941 Effect of Salinity and pH on Pickering Emulsion  
478 Stability. *Society*. 2008;(September):115941-115941. doi:10.2118/115941-MS.
- 479